Patent

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: LARRY L. BRADFORD et al.	Docket No: ACA 6124 PDUS
Serial No: 09/392,434	Examiner: R. Sergent
Filing Date: September 9, 1999	Group Art Unit: 1711
Title: POLYURETHANE FOAM CONTAINING FLAME RETARDANT BLEND OF NON-OLIGOMERIC AND OLIGOMERIC FLAME RETADANTS	

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by
Irwin M. Aisenberg
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[Superscript References are to ENDNOTES in Part III.]

generating an a.c. field . . . a.c. voltage[2184]

A/D

an A/D convertor[10014]

AMP

caused by exogenous cyclic AMP in vitro[9034]

ASTM

ASTM method E-96-80D[8887]

according to ASTM standard D 1238-86[8890]

as measured according to ASTM D813 at room temperature[9005]

Abbe

Abbe's numbers[8882]

Abbreviations, Coined Terms, Names and Symbols

E.g., < >, A, ABS, AC, ACA, ALA, Alpha, Amicon, Ampholien, AO, API, ARG, Arrow, ASP, Asterisk, ASTM, ATCC, ATP, B, BBL, BCG, BET, Beta, BOD, Bordeaux, BPL, Brinell, Bronsted, Brookfield, BTU, C, CEA, CHPO, CI, CNS, COD, Coking, Compana, Conradson, Copiamycin, CYS, D, D & C, Dash, DC, DCA, DE, Delta, DHPO, Diels-Alder, DMN, Dotted Line, Dragendorff, E, EDTA, Ehrlich, Elmendort, EPDM, EPM, EU, F, FD, FD&C, FDP, Fehling, Ferm, Ferrimycin, Fikentscher, Flow, Franklin, Fresnel, Friedel Crafts, Froude, Gamma, Gardner-Holdt, Gatavalin, GLN, GLU, GLY, Hall, Hammet, Hapten, HBS, HIS, HLB, Hydrocarbyl, ILE, IR, K, KEV, KHN, Knoop, Kodak, Kunitz, KV, Laval, LEU, Lewis, LHSV, LYS, M, Mach, Mannich, Marshall, MCA, MCI, MER, MFR, MIL, MIS-FET, Mitocromin, MMSCF, MN, Molisch, Mooney, MOS, MPA, N, Natta, NIH, NMP, NRRL, NSI, Nujol, Oderbrucker, P, Pascal, Pauly PDI, PGR, PH, PHR, PI, PK, pKa, PKS, PLZT, PMR, PN, Poisson, Portland, PP, PPM, Pro, PSI, PSIA, PSIG, R, Raman, Redox, Reynolds, RF, Rockwell, RON, RPM, S, Saybolt, SCF, Schiff, Schopper, Schottky, Sendzimir, Sephadex, Ser, Sermo, Severity, Shore, Sigma, SSU, Sudan, SUS, Tappi, TC, Test, TG, THR, TLC, Tollen, Tolman, TRP, Turpentine, Tyler, TYR, USAF, U.S. SIEVE, UV, V, VAL, VE/VO, Vickers, Washonupana, Wavy Line, Waxy, WHSV, zWijs, X-Ray, Young, Z, Ziegler, ZSM-5.

Aberration

providing color and field aberration correction[9949]

Ablate

to partially ablate vias[9469]

Able (Cf. Capable)

a . . . radical able to impoverish the electronic density of the enolic group . . . by inductive effect[248]

Abnormal

abnormal condition detecting circuit means[9423]

About (Cf. Approximately)

ABOUT: The use of the term "about" permits some leeway in the amount of a required constituent in a claim. Such broadening usages as "about" must be given reasonable scope; they must be viewed by the decision maker as they would be understood by persons experienced in the field of the invention. Although it is rarely feasible to attach a precise limit to "about," the usage can usually be understood in light of the technology embodied in the invention. *Chemical*

[Superscript References are to ENDNOTES in Part III.]

at a pressure in the range of from about 450 to about 950 psi[10290]

value of less than about 35[5789]

above about 100 degrees Centigrade and below about 230 degrees Centigrade[8150]

a melting point above about 40C.[9034]

greater than about 0.05[1955]

overall pressure of 50 to about 800 psia . . . about 30 to about 40 psia (about 2.1 to about 2.8 kg/cm^2)[5817]

within the range of about 0.5 to about 5 microns[14]

from about 0.1 part to about 5 parts by weight . . .; . . . an alkyl radical containing 1 to about 24 carbon atoms[15]

a pH of about 5.6, containing about 6.0 to 7.0% solids, . . . heating . . . to about 70°C. for about one hour, . . . a volume of cooking oil about equal to one volume of the dispersion; . . . shrinks less than about 20%[16]

an amount ranging from about 150 parts by weight to about 1 part by weight . . .; at least about 7% by weight[17]

the range of -20°C. to about 35°C.[18]

Separation Technology Inc. v. United States, 63 U.S.P.Q.2d 1114, 1123, 1124 (U.S. Ct. Fed. Cl. 2002).

See *Elselstein v. Frank*, 34 U.S.P.Q. 1467, 1471 (Fed. Cir. 1995).

See *Conopco Inc. v. May Department Stores Co.*, 32 U.S.P.Q.2d 1225, 1227 (Fed. Cir. 1994).

See *Conopco Inc. v. May Department Stores Co.*, 24 U.S.P.Q.2d 1721 (Mo. 1992).

See *Astral Corp. v. Metcalfe*, (Unpublished) 17 U.S.P.Q.2d 1870, 1872 (Fed. Cir. 1990).

See *Amgen Inc. v. Chugai Pharmaceutical Co. Ltd.*, 18 U.S.P.Q.2d 1016, 1030 (Fed. Cir. 1991). The descriptive term "about" does not render a claim indefinite under 35 U.S.C. 112. The term "about" imparts a broad interpretation to a claimed range. "About" is not broad or arbitrary but rather is a flexible term with a meaning similar to "approximately." As a matter of law, the term "about" is a clear warning that exactitude is not claimed but rather a contemplated variation. *Syntex (U.S.A.) Inc. v. Paragon Optical Inc.*, 7 U.S.P.Q.2d 1001, 1038 (AZ 1987).

Even though this term is often used as a hedge by an applicant, it does not render a claim fatally indefinite. When a range does not have absolute and critical limits and the Patent and Trademark Office (PTO) still requires claims to define the range, a viable compromise is often provided by this hedge. The expression "about" was held [*General Foods Corp. v. Perk Foods Co.*, 157 U.S.P.Q. 14, 32 (D.N.D. Ill. 1968)] to be entitled to latitude in characterizing a feature which was not critical to distinguish over prior art. As a matter of law, the term "about" is a clear warning that exactitude is not claimed but rather a contemplated variation [*Kolene Corp. v. Motor City Metal Treating, Inc.*, 163 U.S.P.Q. 214, 220 (D.E.D. Mich. 1969); aff'd., 169 U.S.P.Q. 77; cert. denied, 171 U.S.P.Q. 325 (U.S. Sup. Ct. 1971)]. Therefore, the phrase "the range of about 1.2-1.8" can cover material with a specific gravity below 1,2 [*Johnson & Johnson v. W. L. Gore & Associates, Inc.*, 181 U.S.P.Q. 597, 598 (D. Del. 1974)]. The descriptive word "about" is not indefinite; it is not unduly broad and arbitrary. Rather, the term is clear, but flexible, and is deemed to be similar in meaning to terms, such as "approximately" or "nearly" [*Ex Parte Eastwood*, Brindle and Kolb, 163 U.S.P.Q. 316, 317 (P.T.O. Bd. App. 1968)].

See *Ex parte George*, et al., 230 U.S.P.Q. 575 (P.T.O. Bd. Pat. App. and Int. 1984).

Cf. *Johnson & Johnson v. W.L. Gore & Associates, Inc.*, 195 U.S.P.Q. 487, 508 (D. Del. 1977).

ABOUT PARTS: See *Jacobson v. Cox Paving Co.*, 19 U.S.P.Q.2d 1641 (Ariz. 1991).

Organophosphorus Compounds

GENNADY M. KOSOLAPOFF
Associate Professor
Alabama Polytechnic Institute

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tions. The transformations that do not involve the phosphorus atom are, as a rule, of such a nature as to be readily apparent to an organic chemist. Such cases are indicated directly in the compound tabulations. The synthetic section of each chapter is followed by a summarization of the general physical and chemical features of the particular class. Exceptions to the general trend are indicated.

Although specific names have been kept to a minimum, for the reason given above, it has been necessary, of course, to make some use of them. The plan adopted in this book differs in some respects from the current practice. It does away with some class names that have been needlessly perpetuated and, it is believed, it brings into closer relationship several compound types set apart by present practice. The names of the discoverers, or of the principal contributors, connected with the major methods of synthesis are given in parentheses following the discussion of the chemistry involved in the particular procedure.

The nomenclature used in this volume is illustrated by the following examples of class and individual names. Customary radical symbols are used for the abbreviated notation in the text.

RPH_2, R_2PH, R_3P. Phosphines; primary, secondary, tertiary. $EtPH_2$—ethylphosphine; EtBuPhP—ethylbutylphenylphosphine. The rather closely related compounds in which a fourth organic radical is linked to phosphorus, probably by semipolar bond, retain the present name of phosphinemethylenes.

RPX_2, R_2PX. Mono- and dihalophosphines. $MePBr_2$—methyldibromophosphine; Ph_2PCl—diphenylchlorophosphine.

RPX_4, R_2PX_3, R_3PX_2. Alkyl-(aryl)phosphorus halides. $EtPCl_4$—ethylphosphorus tetrachloride; Bu_2PCl_3—dibutylphosphorus trichloride.

$RP(O)X_2$, $R_2P(O)X$. Phosphonyl halides; primary, secondary. $EtP(O)Cl_2$—ethanephosphonyl dichloride; EtPhP(O)Br—ethylphenylphosphonyl bromide. Sulfur analogs are named by using the prefix thiono: $MeP(S)Cl_2$—methanethionophosphonyl dichloride.

R_4PX. Quaternary phosphonium compounds. Et_4PCl—tetraethylphosphonium chloride; $MeEt_3POH$—methyltriethylphosphonium hydroxide.

R_3PO. Tertiary phosphine oxides. Pr_3PO—tripropylphosphine oxide. The sulfur and selenium analogs are the sulfides and the selenides, respectively.

$RP(O)(OH)_2$, $R_2P(O)OH$. Phosphonic acids; primary, secondary. $PhP(O)(OH)_2$—benzenephosphonic acid; EtPhP(O)OH—ethylphenylphosphonic acid. The esters are named phosphonates: $MeP(O)(OEt)_2$—diethyl methanephosphonate. The sulfur analogs are named by using

the prefix thio as a noncommittal term in the free acids and in their salts; esters in which there is ample evidence for semipolar link of sulfur to phosphorus are characterized by thiono prefix.

RPO_2H_2. Phosphonous acids. $PhPO_2H_2$—benzenephosphonous acid. The esters are named phosphonites. The sulfur analogs bear the thio prefix.

R_2POH. Phosphinous acids. These compounds are listed as acids provisionally until more direct evidence is secured about their behavior. Et_2POH—diethylphosphinous acid. The esters are named phosphinites. The sulfur analogs are named by using the thio prefix.

$(RO)PX_2$, $(RO)_2PX$. Mono- and dihalophosphites. $EtOPCl_2$—ethyl dichlorophosphite. Sulfur analogs bear the thio prefix: $EtSPBr_2$—(S)-ethyl dibromothiophosphite.

$ROPO_2H_2$, $(RO)_2POH$, $(RO)_3P$. Phosphites; primary, secondary, tertiary. $(EtO)_2POH$—diethyl phosphite; $(PhO)_3P$—triphenyl phosphite. The sulfur analogs are named by using the thio prefix.

$ROP(O)X_2$, $(RO)_2P(O)X$. Halophosphates. $MeOP(O)Cl_2$—methyl dichlorophosphate. The sulfur analogs use the thio prefix for compounds with RS links; the P(S) link is designated by the thiono prefix.

$ROP(O)(OH)_2$, $(RO)_3P(O)OH$, $(RO)_3PO$. Phosphates; primary, secondary, tertiary. $(MeO)_3P(O)OH$—dimethyl phosphate; $(BuO)_3PO$—tributyl phosphate. The sulfur analogs use the thio prefix unless definite proof of the thiono structure is on hand.

The amides of the phosphorous and phosphoric acids are named in the manner indicated by the examples below. $EtOP(O)(NHMe)_2$—ethyl N,N′-dimethyldiamidophosphate; $(PhNH)_2P(O)OH$—N,N′-diphenyldiamidophosphate; Et_2NPCl_2—dichloro-N,N-diethylamidophosphite; $(EtNH)_3PO$—N,N′,N″-triethyl phosphoric triamide; $(EtNH)_3P$—N,N′,N″-triethyl phosphorous triamide.

Imides of phosphorus acids. EtOP:NMe—ethyl N-methylimidophosphite; PhOP(O):NEt—phenyl N-ethylimidophosphate. The sulfur analogs are named as described above.

$RP(O)(NR_2)_2$, $R_2P(O)(NR_2)$. Phosphonamides. $PhP(O)(NHEt)_2$—N,N′-diethyl-benzenephosphondiamide.

R_2PNR_2. Phosphinamides. Et_2PNPr_2—N,N-dipropyl-diethylphosphinamide.

$R_3P{=}NR$. Phosphinimines. Ph_3PNEt—triphenylphosphine-ethylimine.

Quasi-phosphonium compounds. Substances analogous to the true phosphonium compounds and to the phosphorus halides, but containing ester or amide groups. $PhOPCl_4$—phenoxyphosphorus tetrachloride; $(MeO)_2Et_2PI$—dimethoxydiethylphosphorus iodide.

Ullmann's Encyclopedia of Industrial Chemistry

Fifth, Completely Revised Edition

Volume A 19:
Parkinsonism Treatment to Photoelectricity

Editors: Barbara Elvers, Stephen Hawkins, Gail Schulz

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triphenyl phosphite with water, and usually contains considerable quantities of free phenol. A low-phenol product is obtained by reacting triphenyl phosphite with phosphonic acid.

8.6. Alkyl Phosphonates

Alkyl phosphonates are not of great industrial importance, an exception being monoethyl phosphonate, which is marketed as a fungicide in the form of the aluminum salt $Al[C_2H_5OPH(=O)O]_3$ [*39148-24-8*] (Fosetyl-Aluminum, Aliette, Rhône-Poulenc) [8.5], [8.6].

9. Phosphonic Acids and their Derivatives

Of all the various types of organophosphorus compounds, phosphonic acids and their derivatives are outstanding due to their structural variety and great economic importance. Phosphonic acid derivatives are used as crop protection agents (→ Weed Control) in water treatment, in metal processing, and as flameproofing agents.

9.1. Properties

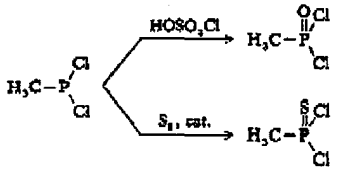
The dibasic phosphonic acids are mostly weaker acids than phosphoric acid. The P—C bond in phosphonic acid derivatives is generally very stable towards oxidation or hydrolysis, so that many reactions can be carried out on the organic part of the molecule. Phosphonic acids are often only slowly biodegradable, but are usually rapidly destroyed by a series of photolytic and biological degradation steps. However, compounds with electronegative substituents on the α-carbon atom are considerably less stable.

Several di- and polyphosphonic acids exhibit complexing (sequestering) properties towards polyvalent cations, and, when added in substoichiometric amounts, prevent the precipitation of low-solubility salts such as alkaline earth sulfates or carbonates (threshold effect).

Esters of phosphonic acid are usually more stable to hydrolysis than the corresponding phosphates, but are converted into free phosphonic acids on heating under acid conditions.

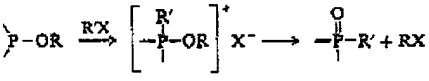
9.2. Production

By Oxidation. The oxidation of low-valency organophosphorus compounds is important mainly in the case of the thiophosphonic acid chlorides. This method is used in the production of methylphosphonic acid dichloride [*676-97-1*] by reaction of methyldichlorophosphine with sulfuryl chloride or chlorosulfuric acid [9.1]. Elemental sulfur reacts with $MePCl_2$ in the presence of catalytic quantities of tetraalkylphosphonium salts [9.2] to form methylthiophosphonic acid dichloride [*676-98-2*].



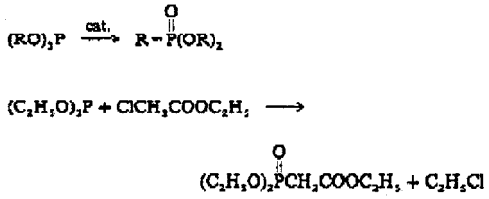
From Organometallic Compounds. Ethylthiophosphonic acid dichloride [*993-43-1*], $C_2H_5P(=S)Cl_2$, is prepared by the reaction of thiophosphoryl chloride with $(C_2H_5)_3Al_2Cl_3$ or $(C_2H_5)_3Al$ (Ethyl process) [9.3], [9.4].

By the Michaelis–Arbusov Reaction. One of the most important reactions in organophosphorus chemistry is the Michaelis–Arbusov reaction, in which compounds containing three-coordinate phosphorus and at least one alkoxy or alkylthio group react with an alkylating agent R′X, forming a phosphorus–carbon bond in compounds with coordination number 4 [9.5], [9.6].



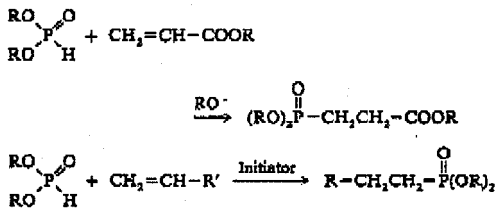
The intermediate phosphonium compounds can only be isolated in exceptional cases. They react further by loss of alkyl halide RX. If R = R′, isomerization occurs with only catalytic quantities of alkylating agent. The method offers a great variety of possibilities, owing to the large range of possible groups R and R′.

Industrially important starting materials for the Michaelis–Arbusov reaction are trialkyl phosphites $P(OR)_3$, which are converted to dialkyl esters of alkanephosphonic acid and to esters of phosphonocarboxylic acids, from which the free phosphonic acids are obtainable by hydrolysis.

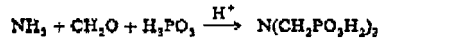


If α-halocarbonyl compounds are used as the alkylating agents, vinyl esters of phosphoric acid are obtained (Perkow reaction, see Chap. 10).

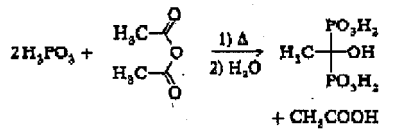
By Addition to C=C Double Bonds. Dialkyl phosphonates undergo base-catalysed addition to activated C=C double bonds. The reaction is mainly used for the production of phosphonocarboxylate esters, and can be carried out as a continuous process [9.7]. In the presence of a radical initiator, nonactivated alkenes can also be used.



By the Quasi-Mannich Reaction. Phosphonic (phosphorous) acid H_3PO_3 or its dialkyl esters react with mixtures of formaldehyde with ammonia or amines under acidic conditions to give oligo(methylenephosphonates). When oligo(ethylene)amines are used, the industrially important poly(methylenephosphonic acids) are formed.



By Acylation of Phosphonic Acid. The reaction of phosphonic acid with acetyl chloride or acetic anhydride yields 1-hydroxyethane-1,1-diphosphonic acid [*2809-21-4*] after hydrolysis.



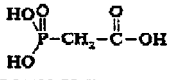
Alternative starting materials are PCl_3 and acetic acid in the presence of water [9.8].

The reaction can also be carried out with other carboxylic acid derivatives [9.9]–[9.12]. For example, with acetonitrile, 1-aminoethane-1,1-diphosphonic acid [*15049-85-1*] is obtained.

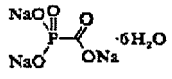
9.3. Phosphonic Acids and Phosphonocarboxylic Acids

Methylphosphonic acid [*993-13-5*] (Ciba-Geigy) is used in the production of lubricant additives and for treating textiles [9.13], [9.14]. Octylphosphonic acid [*4724-48-5*] (Hoechst) is used as a selective collector for the flotation of cassiterite (tin ore). Vinylphosphonic acid [*1746-03-8*] (Hoechst) [9.15], [9.16] or its polymers are used for the surface treatment of aluminum in the manufacture of printing plates [9.17]. Phenylphosphonic acid [*1571-33-1*] (Akzo) is used as a catalyst in the production of resins and for manufacturing stabilizers for plastics.

Salts of phosphonoformic acid and phosphonoacetic acid (**5**) have virostatic properties. Trisodium phosphonoformate (**6**) (Foscarnet) is used in the treatment of herpes (Triapten, formerly VEB Germed) or cytomegalic infections in humans (Foscavir, Astra).

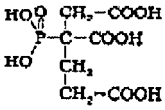


5 [*4408-78-0*]



6 [*34156-56-4*]

2-Phosphonobutane-1,2,4-tricarboxylic acid (**7**) [*37971-36-1*] (NH_4 salt [*70233-62-4*], Bayhibit AM, Bayer) is used in industrial water treatment on account of its complexing properties.

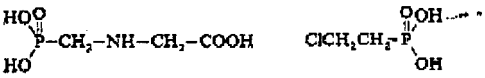


7 [*37971-36-1*]

Geminal diphosphonic acids are used in the same application, and in washing and cleaning agents, peroxide stabilizers, and many other areas. Compounds of this type include 1-hydroxyethane-1,1-diphosphonic acid [*2809-21-4*] (Briquest ADPA, Albright & Wilson; Sequion 10 H 60, Bozetto; Turpinal SL, Henkel; Jaypol 210, M & J Polymers; Dequest 2010/2016, Monsanto; Mykon P60, Warwick) and 1-aminoethane-1,1-diphosphonic acid [*15049-85-1*] (BK Laden-

burg), as well as the large group of poly(methylenephosphonic acids) produced from ammonia or ethylene amines. Some important products are nitrilotris(methylenephosphonic acid) [*6419-19-8*], ethylenediaminetetrakis(methylenephosphonic acid) [*1429-50-1*] and diethylenetriaminepentakis(methylenephosphonic acid) [*15827-60-8*]. Producers (trade names) are: Albright & Wilson (Briquest), Bozetto (Sequion), M&J Polymers (Jaypol), Monsanto (Dequest).

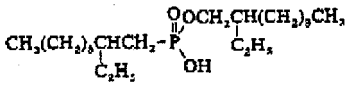
The total herbicide *N*-carboxymethylaminomethanephosphonic acid (*N*-phosphonomethylglycine) [*1071-83-6*], Glyphosate (Roundup, Monsanto) is outstanding for its effectiveness and ease of biodegradability. It is used in the form of its isopropylammonium salt [*38641-94-0*]. The sodium salt of 2-chloroethylphosphonic acid [*16672-87-0*] Ethepon (Ethrel, Union Carbide) causes accelerated ripening of fruit by releasing the ripening hormone ethylene in the plant.



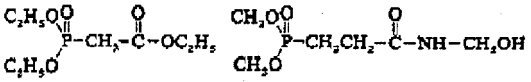
[*1071-83-6*] [*16672-87-0*]

9.4. Esters of Phosphonic Acid

Monoesters of phosphonic acid are used in industry only to a limited extent. Salts of short-chain alkyl alkylphosphonates have a flameproofing effect [9.18], [9.19]. The 2-ethylhexyl ester of 2-ethylhexylphosphonic acid (**8**) (PC-88A, Daihachi; Ionquest 801, Albright & Wilson) is used as an extractant for lanthanides and for the separation of cobalt and nickel [9.20].



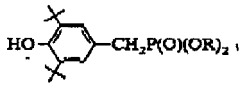
8 [*14802-03-0*]



9 [*867-13-0*] **10** [*20120-33-6*]

Dialkyl alkylphosphonates are used as flameproofing agents, metal extractants, plasticizers, lubricant additives, and chemical intermediates. The more important compounds are listed in Table 10 with their physical properties. Producers of the methyl compound DMMP include Akzo, Albright & Wilson, Bayer, Ciba-Geigy, and Courtaulds. Other compounds are produced by Albright & Wilson and Daihachi.

Diethyl ethoxycarbonylmethylphosphonate (**9**) (triethyl phosphonoacetate; PEE, Hoechst) is used as a stabilizer for polyesters [9.21]. Esters of phenylmethylphosphonic acid with bulky substituents (Irganox 1222 [*976-56-7*] and 1093 [*3135-18-0*], Ciba-Geigy) are sold as antioxidants and high-temperature stabilizers for polyamides, polyesters, polyolefins and polyurethane foams.



R = C_2H_5; [*976-56-7*]
R = $C_{18}H_{37}$; [*3135-18-0*]

A wide range of other phosphonate esters, often containing chlorine, are used as flameproofing agents. Producers (trade names) are: Akzo (Fyrol, Victastab), Albright & Wilson (Amgard, Antiblaze), Sandoz (Sandoflam 5087). Dimethyl 3-hydroxymethylamino-3-oxopropanephosphonate (**10**) is of particular importance in the production of washable flameproofed cellulose textiles (Pyrovatex CP, Ciba-Geigy) [9.22]–[9.24].

Table 10. Physical properties of dialkyl alkyl phosphonates $RP(=O)(OR)_2$

R	CAS no.	M_r	Density, g/cm³	*bp* (*p*), °C (Pa)	n_D^{20}	Flash point, °C
CH_3	[*756-79-6*]	124.08	1.174	62 (1330)	1.4137	92[a]
C_2H_5	[*78-38-6*]	166.16	1.025	82 (1433)	1.4148	90[b]
$CH_2CH_2CH_2CH_3$	[*78-46-6*]	250.32	0.948	127 (330)	1.4310	125[c]
$CH_2CH(CH_2)_3CH_3$ C_2H_5	[*126-63-6*]	418.64	0.908	160 (33)	1.4483	158[c]

[a] Pensky–Martens closed cup. [b] Tag closed cup. [c] Cleveland open cup.

9.5. Other Derivatives of Phosphonic Acid

Halides of phosphonic and thiophosphonic acids are mainly used in the synthesis of crop protection agents. Ethylthiophosphonic acid dichloride is used in the production of the insecticide Fonofos [*944-22-9*] (Dyfonate, ICI) and Trichloronat [*327-98-0*] (Agrisil, Phytosol, Bayer), and benzenethiophosphonic acid dichloride [9.25] in the production of *O*-2,4-dichlorophenyl *O*-ethyl phenylphosphonothioate (S-Seven) [*3792-59-4*] and EPN [*2104-64-5*] (both Nissan Chemical Industries).

The acid halides are produced by Akzo, Ethyl, Ferro, and Nissan Chemical Industries. Physical properties are listed in Table 11.

10. Esters of Phosphoric Acid

The esters of phosphoric acid constitute an important group of organophosphorus compounds with a broad application as cleaning agents and emulsifiers, textile improvers, plasticizers and flameproofing agents for plastics, anticorrosion agents, and extractants in hydrometallurgy [6.46]–[6.49]. Phosphoric acid ester chlorides are starting materials in the production of crop protection agents. Many vinyl esters of phosphoric acid have insecticidal properties (→ Insect Control, A14, p. 285–286).

10.1. Properties

Phosphate esters are colorless liquids or crystalline or waxy solids, depending on the substituents. The triesters are neutral compounds, while the mono- and diesters are strongly acidic. The esters of phosphoric acid hydrolyze in the presence of water. The rate of hydrolysis varies widely and depends on the degree of esterification and the nature of the substituents.

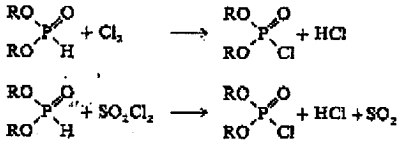
10.2. Production

The important raw materials for the production of esters of phosphoric acid are phosphoryl chloride, phosphorus pentoxide, polyphosphoric acid, and trialkyl phosphites.

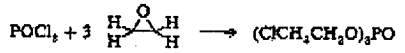
Phosphorus oxychloride reacts with phenols to form triaryl phosphates. With aliphatic alcohols, the hydrogen chloride formed must be removed by vacuum or by purging with an inert gas. Alternatively, bases may be added.

$$POCl_3 + 3\,ROH \longrightarrow (RO)_3PO + 3\,HCl$$

If a substoichiometric amount of alcohol is used, ester chlorides of phosphoric acid are formed. However, diester chlorides of phosphoric acid are better obtained by reacting dialkyl phosphonates with chlorine or sulfuryl chloride.



The addition of ethylene oxide or propylene oxide to $POCl_3$ at 40–100 °C affords tris(2-chloroethyl) or tris(2-chloropropyl) phosphate. To ensure complete reaction, catalysts must be added ($AlCl_3$, $TiCl_4$, PCl_3).



A mixture of mono- and diesters is formed when alcohols or phenols are reacted with phosphorus pentoxide, while the reaction with polyphosphoric acid yields monoesters of phosphoric acid and free phosphoric acid.

Table 11. Physical properties of phosphonic and thiophosphonic acid halides

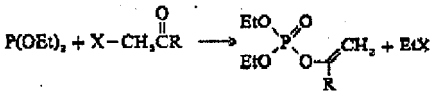
Formula	CAS no.	M_r	Density, g/cm³	*bp* (*p*), °C (Pa)	n_D^{20}	Flash point, °C
$CH_3P(O)Cl_2$	[*676-97-1*]	132.91	1.39[a]	163 (1.03×10^5)	1.462[a]	>110
$C_6H_5P(O)Cl_2$	[*824-72-6*]	194.99	1.394	258 (1.03×10^5)	1.5600	204[b]
$CH_3P(S)Cl_2$	[*676-98-2*]	148.98	1.434	154 (1.03×10^5)	1.548	76[b]
$C_2H_5P(S)Cl_2$	[*993-43-1*]	163.01	1.35	172 (1.03×10^5)	1.541	74[b]
$C_6H_5P(S)Cl_2$	[*3497-00-5*]	211.04	1.376	205 (1.73×10^4)	1.6240	>110

[a] At 38 °C. [b] Cleveland closed cup.

$$P_4O_{10} + 6\,ROH \longrightarrow 2(RO)_2PO(OH) + 2\,ROPO(OH)_2$$

$$H_6P_4O_{13} + 3\,ROH \longrightarrow 3\,ROPO(OH)_2 + H_3PO_4$$

An important method for the production of insecticidal vinyl phosphates is the reaction between trialkylphosphites and α-halocarbonyl compounds (Perkow Reaction) [10.1].



10.3. Trialkyl Phosphates

Table 12 gives a survey of the important trialkyl phosphates.

Triethyl phosphate is used as a catalyst in the production of acetic anhydride by the ketene process, as a desensitizing agent for peroxides, and as a solvent and plasticizer for cellulose acetate. Tributyl phosphate is used for solvent extraction in hydrometallurgy. Tris(2-ethylhexyl) phosphate is used as a solvent in the production of hydrogen peroxide and is also used as a plasticizer with flameproofing properties. The important producers of trialkyl phosphates are Akzo, Albright & Wilson, Bayer, Daihachi Chemical Industry, and FMC.

Tris(chloroalkyl) phosphates are used as fire retardants for polyurethane foams, polyesters, and other plastics [10.2]. In addition to the compounds listed in Table 12, a large number of other halogen-containing, sometimes oligomeric trialkyl phosphates with mixed ester groups are marketed as flameproofing agents. Producers (trade name) are: Albright & Wilson (Amgard), Akzo (Fyrol), Bayer (Disflamoll), Courtaulds, Great Lakes Chemical Corp. (Firemaster), Hoechst (Genomoll), Olin (Thermolin), and Sandoz (Sandoflam).

10.4. Triaryl and Alkyl Aryl Phosphates

Some important aromatic triesters of phosphoric acid are listed in Table 13.

These compounds are mainly used as flameproofing and plasticizing agents for plastics, as lubricants, and as low-flammability hydraulic fluids. Mixtures of isomers are mainly used, based on technical-grade alkyl phenols.

Some producers (trade names) are: Akzo (Phosflex), Albright & Wilson (Pliabrac), Bayer (Disflamoll), Ciba-Geigy (Reofos), FMC (Kronitex), Monsanto (Santicizer).

10.5. Mono- and Dialkyl Phosphates

Only a small number of pure compounds in this class are of industrial importance. Bis(2-ethylhexyl) phosphate [*298-07-7*] DEHPA, is used in hydrometallurgy as an extraction solvent for a large number of metals. It is produced by chlorinating bis(2-ethylhexyl) phosphonate [*3658-48-8*] to give the phosphate diester chloride, followed by hydrolysis [10.3], or by saponification of tris(2-ethylhexyl) phosphate [*78-42-2*]. It is produced by Albright & Wilson, Bayer, Daihachi, and Hoechst. Products with a high monoester content, obtained from ethoxylated alcohols, are used as defoamers in washing powders (Sokalan S, BASF).

Table 12. Physical properties of trialkyl phosphates $(RO)_3PO$

R	CAS no.	M_r	Density, g/cm³	*bp* (*p*), °C (Pa)	n_D^{20}	Flash point, °C
CH_3	[*512-56-1*]	140.08	1.197	197 (1.03×10^5)	1.3960	none
C_2H_5	[*78-40-0*]	182.16	1.064	215 (1.03×10^5)	1.4039	116
CH_2CH_2Cl	[*115-96-8*]	285.51	1.414	210–220 (2700)	1.4720	252[a]
$CH(CH_3)CH_2Cl$	[*13674-84-5*]	327.57	1.294	[b]	1.4625	218[a]
$CH(CH_2Cl)_2$	[*13674-87-8*]	430.91	1.513	[b]	1.5019	251[a]
$CH_3(CH_2)_2CH_2$	[*126-73-8*]	266.32	0.976	148–153 (1330)	1.4249	165[a]
$CH_2CH_2OC_6H_5$	[*78-51-3*]	398.48	1.006	215–228 (532)	1.4380	224[a]
$CH_2CH(CH_2)_3CH_3$ | C_2H_5	[*78-42-2*]	434.64	0.924	196–200 (133)	1.4440	193[a]

[a] Cleveland open cup. [b] Decomposes.

Table 13. Physical properties of triaryl phosphates $(R^1O)_3PO$ and alkyl aryl phosphates $(R^1O)(R^2O)_2PO$

R^1	R^2	CAS no.	M_r	Density, g/cm³	bp (p), °C (Pa)	n_D^{20}	Flash point, °C
C_6H_5		[115-86-6]	326.29		244 (1330)		223
$C_6H_4CH_3$		[1330-78-5]	368.37	1.17	249 (533)	1.555	252
$C_6H_3(CH_3)_2$		[25155-23-1]	410.45	1.147	248–265 (533)	1.553	263
$C_6H_4CH(CH_3)_2$		[68937-41-7]	452.53	1.16	220–270 (533)	1.552	254
$CH_2CH(CH_2)_3CH_3$ C_2H_5	C_6H_5	[1241-94-7]	362.41	1.09	239 (1330) decomp.	1.508	224
iso-$C_{10}H_{21}$	C_6H_5	[29761-21-5]	390.46	1.07	245 (1330) decomp.	1.507	241
$C_6H_4CH_3$	C_6H_5	[26444-49-5]	340.32	1.20	235–255 (1330)	1.561	230
$C_6H_4C(CH_3)_3$	C_6H_5	[56803-37-3]	385.42	1.18	258 (1330)	1.555	263

Esters of thiophosphoric acid are used in plant protection (→ Insect Control; → Fungicides, Agricultural A 12, pp. 98–99) and as flotation agents in ore preparation, lubricant additives, for solvent extraction of metals, and in rubber production.

Mixtures of mono- and diesters of phosphoric acid are of major industrial importance. Their properties can be varied over a wide range by choice of the alcohol or phenol. Ethoxylated alcohols are most commonly used. The wide range of applications includes emulsifiers in plant protection, cleaning agents, cosmetics, and in the paper and textile industries. Mixtures of mono- and diesters are also used as acid hardeners for resins. Manufacturers (trade names) include Akzo (Dapral, Victawet), Albright & Wilson (Albrite, Briphos, Duraphos), GAF (Gafac), Henkel (Disponil), Hoechst (Hostaphat, Leomin, Knapsack phosphate esters), Hüls (Marlophor), and Rhône-Poulenc (Celanol, Soprophor).

Mixtures of monoesters of phosphoric acid with free phosphoric acid are also marketed. These are mainly used as components of detergents (Hoechst).

11. Esters of Thiophosphoric Acid

The esters of thiophosphoric acid are formally derived by the replacement by sulfur of one or more of the oxygen atoms bonded to phosphorus in esters of phosphoric acid. Thiophosphoric acids form mono-, di-, and triesters, the location of the organic substituent being indicated as *O*- or *S*-. Of the large range of possible compounds, the derivatives of mono- and dithiophosphoric acid have attained the greatest industrial importance.

11.1. Properties

Thiophosphate esters generally have an unpleasant smell and in the pure state are colorless liquids or solids. The triesters are neutral, while the mono- and diesters are strongly acidic. Technical-grade *O,O*-dialkyl dithiophosphates usually have a greenish or yellowish color due to traces of heavy metals. The short-chain compounds in particular cannot be stored indefinitely, and are usually immediately converted into other products. The thermal and hydrolytic stability increases with increasing alkyl chain length and degree of esterification and upon salt formation, so that diaryl dithiophosphates are more easily hydrolyzed than alkyl esters of comparable chain length [11.1].

Many esters of thiophosphoric acid have high biological activity as acetylcholine esterase inhibitors and are therefore useful insecticides. However, the toxicity to warm-blooded animals is very high. The compounds are decomposed to less toxic products on contact with the soil, as they are readily hydrolyzed.

11.2. Production

Important raw materials for the production of esters of thiophosphoric acid include phosphorus pentasulfide, thiophosphoryl chloride, and dialkyl hydrogenphosphonates.

Phosphorus pentasulfide reacts with alcohols or phenols with loss of H_2S to form the industrially important *O,O*-diesters of dithiophosphoric acid. Addition of catalytic nitrogen, phosphorus, or sulfur compounds (e.g., phosphonium halides) improves the yield of the reaction and the product quality [11.2]–[11.4].

$P_4S_{10} + 8ROH \longrightarrow$

In practice, a susper
tasulfide in the end proc
alcohol at 60–80 °C. D
ty, phenols must be re
hydrogen sulfide produ
fur dioxide formed is re
alkali.

O,O-Dialkyl esters
are converted to *O,O*-
phosphoric acid by
Depending on the condi
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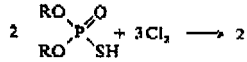
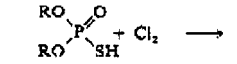
[10025-67-9] or sulfur.





Another route to thi
the reaction of thiophos
cohols in the presence o

$PSCl_3 + 2ROH \longrightarrow$

Salts of thiophospho
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O,O-diesters of thiopho
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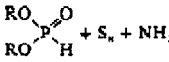
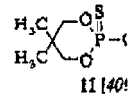
phoric acid.

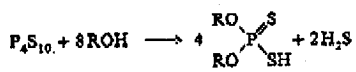


11.3. Monothiophos

O,O-Diesters of thio
as extraction solvents fo
ly zinc, or as lubricant ac
of thiophosphoric anh
5060, Sandoz) is used
proofing agent for lo
films.

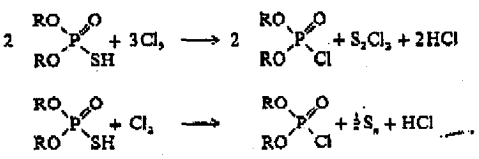


11 [40

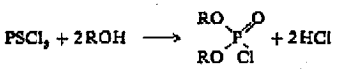


In practice, a suspension of phosphorus pentasulfide in the end product is reacted with excess alcohol at 60–80 °C. Due to their lower reactivity, phenols must be reacted at 80–120 °C. The hydrogen sulfide produced is burnt, and the sulfur dioxide formed is removed by scrubbing with alkali.

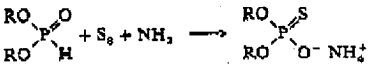
O,O-Dialkyl esters of dithiophosphoric acid are converted to *O,O*-diester chlorides of thiophosphoric acid by reaction with chlorine. Depending on the conditions, the byproducts are hydrogen chloride and disulfur dichloride [*10025-67-9*] or sulfur.



Another route to this class of compounds is the reaction of thiophosphoryl chloride with alcohols in the presence of acid acceptors.

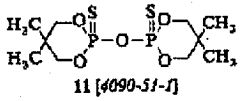


Salts of thiophosphoric acid are produced by reacting dialkyl hydrogenphosphonates with sulfur in the presence of a base (e.g., ammonia). The *O,O*-diesters of thiophosphoric acid are liberated from these compounds by reaction with phosphoric acid.



11.3. Monothiophosphates

O,O-Diesters of thiophosphoric acid are used as extraction solvents for heavy metals, especially zinc, or as lubricant additives. The *O,O*-diester of thiophosphoric anhydride (**11**) (Sandoflam 5060, Sandoz) is used as a halogen-free flameproofing agent for low-density polyethylene films.



11 [*4090-51-1*]

The alkylation of *O,O*-dialkyl thiophosphates usually gives mixtures of *O,O,O*- and *O,O,S*-triesters of thiophosphoric acid, some of which are used in crop protection.

The *O,O*-diester chlorides of thiophosphoric acid are very important in the synthesis of crop protection agents, and are usually reacted with phenols or their salts to give insecticidal or fungicidal *O,O,O*-triesters of thiophosphoric acid (Parathion [*56-38-2*], Methylparathion [*298-00-0*] → Insect Control; Pyrazophos [*13457-18-6*] → Fungicides, Agricultural). The most important intermediates are *O,O*-dimethoxylthiophosphoryl chloride [*2524-03-0*], $(CH_3O)_2PSCl$, M_r 160.56, *bp* 70–72 °C (270 Pa), ϱ 1.305 g/cm³, n_D^{20} 1.4807, flash point 101 °C, colorless liquid (Cheminova), and *O,O*-diethoxylthiophosphoryl chloride [*2524-04-1*], $(C_2H_5O)_2PSCl$, M_r 188.61, *bp* 71–72 °C (93 Pa), ϱ 1.200 g/cm³, n_D^{20} 1.4688, flash point 106 °C, colorless liquid (Albright & Wilson, Cheminova).

11.4. Dithiophosphates

The *O,O*-diesters of dithiophosphoric acid and aqueous solutions of sodium or ammonium dithiophosphates are used as flotation agents for sulfidic copper and cadmium ores. A new application of increasing importance is the extraction of cadmium from wet phosphoric acid by formation of insoluble complex salts [11.5]–[11.7]. The *O,O*-dialkyl dithiophosphates of short to medium chain length (C_2–C_8) are particularly effective in this application. The amount added is ca. 0.3 %, depending on the origin of the crude phosphoric acid and the temperature. Preliminary reduction of the acid with iron improves the efficiency of separation of the cadmium [11.8].

The zinc salts of long-chain esters are used as lubricant additives to improve high-pressure lubrication properties, and useful life of the lubricant [11.9] (→ Lubricants, A 15, p. 451). They are produced by reacting zinc oxide with the alcohol-containing *O,O*-diesters of dithiophosphoric acid. The crude product is recovered by pressure filtration, and the water liberated in the reaction and the excess alcohol are then removed by vacuum distillation.

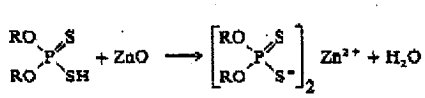


Table 14. Physical properties *O,O*-dialkyl dithiophosphates $(RO)_2P(S)SH$

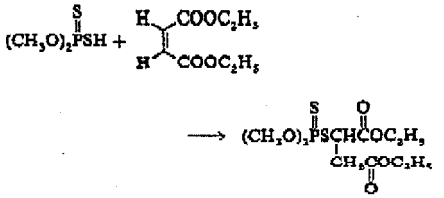
R	CAS no.	M_r	Density, g/cm³	*bp* (*p*), °C (Pa)	n_D^{20}	Flash point, °C
CH_3	[*756-80-9*]	158.19	1.28	48 (270)	1.5350	92
C_2H_5	[*298-06-6*]	186.23	1.17	85 (650)	1.5070	82[a]
$CH(CH_3)_2$	[*107-56-2*]	214.29	1.10	90 (400)	1.4933	112[a]
$CH_2CH(CH_3)_2$	[*2253-52-3*]	242.34	1.05	107 (300)	1.4908	136[a]
$CH(CH_3)C_2H_5$	[*107-55-1*]	242.34	1.07	100 (200)	1.4928	79[b]
$CH_2CH(CH_2)_2CH_3$ C_2H_5	[*5810-88-8*]	354.56	0.98		1.4855	180[a]

[a] Cleveland open cup. [b] Pensky–Martens closed cup.

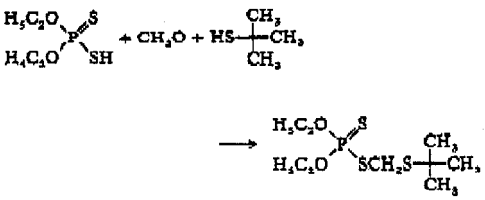
These products protect the metal surface by forming a sulfide and thiophosphate layer, by removing oxidation products from the lubricant, and by corrosion inhibition.

Water-insoluble *O,O*-dialkyl esters of dithiophosphoric acid can be used as extractants for the hydrometallurgical removal of heavy metals such as zinc from dilute acidic solutions, and are therefore of interest for the treatment of wastewater and polluted groundwater.

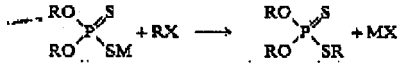
An important reaction of *O,O*-dialkyl dithiophosphates is the addition of an activated C=C double bond to form *O,O,S*-triesters of dithiophosphoric acid. Thus, *O,O*-dimethyl dithiophosphate [*756-80-9*] and diethyl maleate react to produce the insecticide Malathion [*121-75-5*].



The addition to C=O double bonds is the key reaction in the synthesis of the insecticide Terbufos [*13071-79-9*] from *O,O*-diethyldithiophosphoric acid [*298-06-6*], formaldehyde, and 2-methyl-2-propanethiol [*75-66-1*].



O,O-Dialkyl dithiophosphates are alkylated at the sulfur atom by alkyl halides. This reaction is used to produce numerous insecticidal *O,O,S*-triesters of dithiophosphoric acid.



Alkyl Dithiophosphates. The physical properties of the most important *O,O*-dialkyldithiophosphoric acids are given in Table 14.

Most long-chain compounds are produced from mixtures of alcohols. Manufacturers include Albright & Wilson, American Cyanamid, Cheminova, and Hoechst. Aqueous solutions of the salts are marketed as flotation agents by American Cyanamid (Aerofloat) and Hoechst (Hostaflot). Lubricant additives based on the zinc salt are supplied by Chevron and Lubrizol.

Aryl Dithiophosphates. An important compound of this type is dicresyldithiophosphoric acid [*27157-94-4*] $(CH_3C_6H_4O)_2P(S)SH$ (M_r 279.41, brown liquid), used as a flotation agent for sulfidic ores. The commercial product is not usually a pure substance, being the reaction product of a mixture of phenol, cresols, and xylenols with phosphorus pentasulfide. Both the free acid and an aqueous solution of the ammonium salt are commercial products (Aerofloat 25, 31, 242, American Cyanamid; Phosokresol B, C, E, Hoechst).

12. Economic Aspects

Measured by the tonnage of inorganic phosphorus-containing base materials, e.g., PCl_3 and $POCl_3$, used in their production, the organophosphorus products discussed here are of minor importance. Based on value, the comparison is